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1.	Your reference	IP/F7223
2.	Patent application number *(The Patent Office will fill in this part)*	0224179.2 17 OCT 2002
3.	Full name, address and postcode of the or of each applicant *(underline all surnames)*	ZBD Displays Ltd Malvern Hills Science Park Geraldine Road, Malvern, Worcestershire WR14 3SZ United Kingdom
	Patents ADP number *(if you know it)*	841891 5001
	If the applicant is a corporate body, give the country/state of its incorporation	GB
4.	Title of the invention	LIQUID CRYSTAL ALIGNMENT
5.	Name of your agent *(if you have one)*	PHILIP DAVIES 'et al'
	"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	QINETIQ LIMITED IP Formalities A4 Bldg Cody Technology Park Ively Road Farnborough Hants GU14 0LX United Kingdom
	Patents ADP number *(if you know it)*	831241 5001

		Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*
6.	If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number			

		Number of earlier application	Date of filing *(day / month / year)*
7.	If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application		

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:*
   - *a) any applicant named in part 3 is not an inventor, or*
   - *b) there is an inventor who is not named as an applicant, or*
   - *c) any named applicant is a corporate body. See note (d))*

   YES (b)

9. Enter the number of sheets for any of the following items you are filing with this form. Do not count copies of the same document

Continuation sheets of this form	0
Description	14 TW
Claim(s)	0
Abstract	0
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10. If you are also filing any of the following, state how many against each item.

Priority documents	0
Translations of priority documents	0
Statement of inventorship and right to grant of a patent *(Patents Form 7/77)*	0
Request for preliminary examination and search *(Patents Form 9/77)*	0
Request for substantive examination *(Patents Form 10/77)*	0
Any other documents *(please specify)*	0

11. I / We request the grant of a patent on the basis of this application.

Signature [signature] PHILIP DAVIES

Date 17.10.02

12. Name and daytime telephone number of person to contact in the United Kingdom — Linda Bruckshaw 01252 392722

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Notes

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LIQUID CRYSTAL ALIGNMENT

This invention relates to blending monomers, oligomers, and other additives such that the resulting photopolymer has the desired optimal physical, optical, electrical, and chemical properties for the manufacture of and the electrical switching of ZBD devices of the type described in EP0856164.

1 Background

Currently, the diffraction grating structure within a ZBD cell is fabricated by hard contact photolithography in a deep UV photoresist. A simpler and higher throughput method for manufacture is to emboss from a master grating onto a second material which is printed onto the glass substrate. This is described in more detail in patent application 02253326.9 (case re P7139). The second material could be in the form of a UV curable photopolymer. It is printed or nip fed onto the glass. A flexible carrier film or a nickel/polymer shim is used as the master grating. Pressure is applied to the carrier film or shim so that the photopolymer flows and forms a film of around *1-1.5* micron. The photopolymer is exposed to UV light which causes it to solidify. The carrier film or shim is then removed from the glass leaving behind the textured polymer film. The adhesion properties of the photopolymer are critical to control. The photopolymer must adhere well the glass/ITO yet release cleanly from the carrier film/shim. In addition since the polymer is in contact with the LC within the cell, the chemical, physical, optical, and electrical properties are crucial properties to control. Important properties include

Release from carrier film/shim but good adhesion to glass/ITO
Refractive index
Optical absorption
Surface energy
Ability to be post treated with a surfactant (e.g silane or alcohol treatment)
Viscosity
Polymerization speed

Shrinkage
Ionic content
Dielectric permittivity

62 Invention

There are many photopolymers that have a refractive index equal to n_o of the current liquid crystal (n_0=1.504). However, they generally do not have low viscosity and the correct surface energy to align the LC (and indeed all of the other desirable physical, chemical, electrical and optical properties). To be able to control and vary these properties independently it is proposed that monomers, oligomers, and additives are blended together to make a composite photopolymer. Monomer content decreases viscosity but increases shrinkage. Oligomer content decreases shrinkage but increases viscosity and to a large extent controls the physical properties. Both are readily available in a variety of refractive indexes.

83 Examples of property control

1. Optimising refractive index

Sample preparation

A master was made by first coating an ITO coated glass substrate with UVIII, a deep UV resist. This was achieved by spin coating at 1100 rpm in a gyroset spin coater. After a suitable soft bake to remove solvent it was placed in hard contact with a chrome on glass mask and exposed to collimated UV light for 9 seconds. The chrome on glass mask consisted of 0.35 micron chrome lines with a repeat period of 1 micron. After an activation bake the resist was developed and washed in di-ionised water. It was then exposed in an EPROM eraser and baked in a vacuum oven for 2.5 hours at 173 degrees. The surface was then treated with a fluorinated polymer called CYTOP. This was spin coated at 3000 rpm at a dilution of 1:3 in perfluorotributylamine. The substrate had a further 1 hour bake at 160 degrees.

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Dear Sirs

Please find attached Patent Application for the above case. I would be grateful if you would fax the reply to

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Yours faithfully

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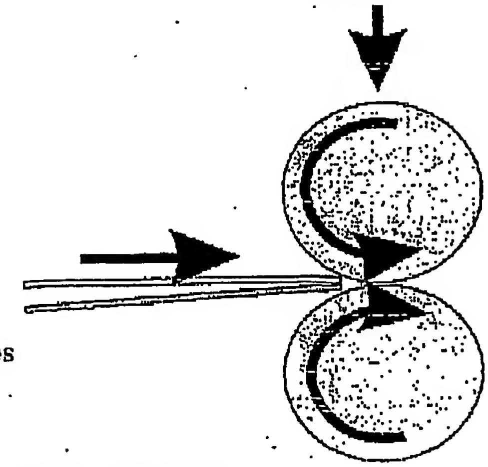

Figure 1 Simple lamination apparatus

The substrate consisted of an ITO coated 0.55 mm thick glass substrate. This was cleaned with solvents and placed in a UV Ozone chamber for 10 minutes to render the surface high energy. Small drops of photopolymer were placed on the substrate and the master placed on top. The laminate was then passed between a pair of soft rollers as shown in the above diagram. The shore hardness of the rollers was shore hardness 'D'. The compression of the rollers was 1.8 mm and the speed was 2 mm/sec. The laminate was then cured under an UV lamp and separation was achieved by peeling away the master with a blade. Cells were made by treating the photopolymer and assembling against a rubbed poly-imide substrate. They were filled with MLC6204-000.

In order to maintain maximum brightness of the display the optical absorption of the grating polymer should be minimized. In addition it is desirable to reduce/remove diffraction effects in the reflected (undiffracted) beam. Two configurations are possible for the orientation of the polariser which is adjacent to the grating surface:

1. E- Mode (P polarised)
2. O-Mode (S polarised)

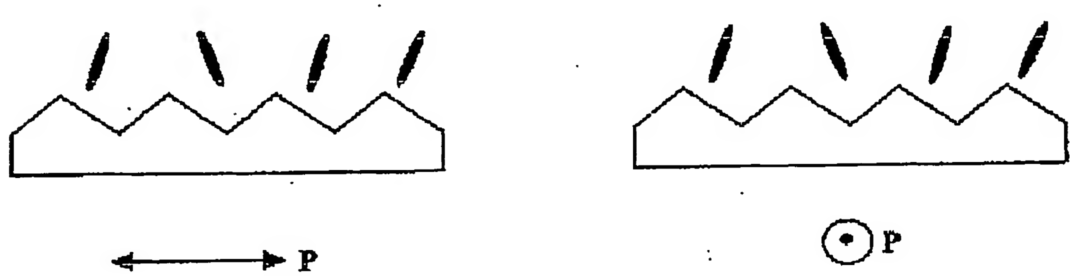

Figure 2 Two possible polariser orientations for a ZBD cell.

In configuration 1, the input polarisation samples n_e and n_o of the LC which cannot both be matched to the refractive index of the grating polymer (n_p). Hence the grating LC interface can never be optically buried and diffraction will always exist. In configuration 2, the input polarisation only samples n_0 of the LC and so the grating diffraction can be removed completely (at normal incidence) when $n_p=n_o$. Furthermore this matching condition is retained for both the D and ND states. For off axis viewing, the diffraction will start to appear in the plane parallel to the groove direction but will remain zero for the orthogonal plane.

Reflectivity data was taken on an Eldim Ezcontrast 160R machine. Two cells were examined, one where the grating was made in photoresist, the other where the grating was made by embossing into a silicone hard coat material (GE silicones UVHC 8556). The reflectivity data is shown in table 1 and the refracting index in table 2.

Front Polariser	Back Polariser	Grating polymer	Mode	Reflectivity	Contrast
HEG1425DUHCARS	TDF	UVIII	o	0.315	14.1
HEG1425DUHCARS	TDF	Embossed	o	0.330	>20

Table 1 Reflectivity data for a resist and an embossed cell

Material name	Material type	n (589nm)
Shipley UVIII	Polyhydroxylstyrene photoresist	1.541
GE UVHC8556	Acrylate silicone photopolymer	1.514

Table 2 Refractive index data for a resist and an embossed cell.

The refractive index n_o of MLC6204-000 is 1.504. The results above show that the reflectivity and contrast is improved for the embossed cell due to the fact that the refractive index is closer to n_0 compared to resist. This decreases diffractive losses within the cell.

The refractive index can be controlled by mixing, for example, two monomers that have different refractive indexes. The refractive index of the mixture is a linear weighting of the percentage of each material. For example, monomer actilane 420 has n=1.537, and actilane 425 n=1.457. A blend of 59% actilane 420 and 41% actilane 425 would have a refractive index of 1.504. Figure 3 shows the refractive index of the mixture as a function of composition. The viscosity of the mixture can be controlled in a similar fashion (different functional dependence on concentration).

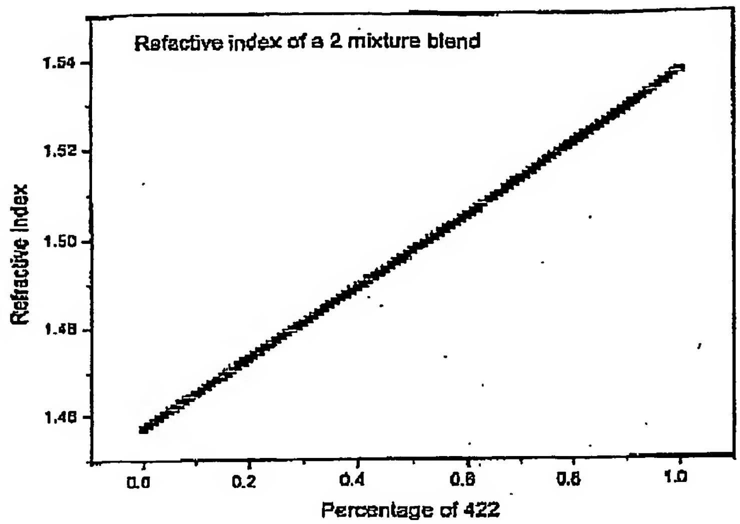

Figure 3 The refractive index as a function of concentration of 422 in 425

2. Modification of release and adhesion

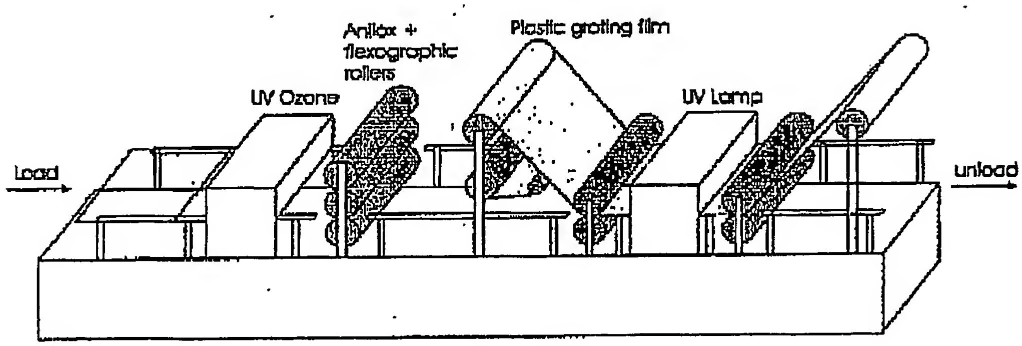

Figure 4 Carrier film onto glass embossing machine

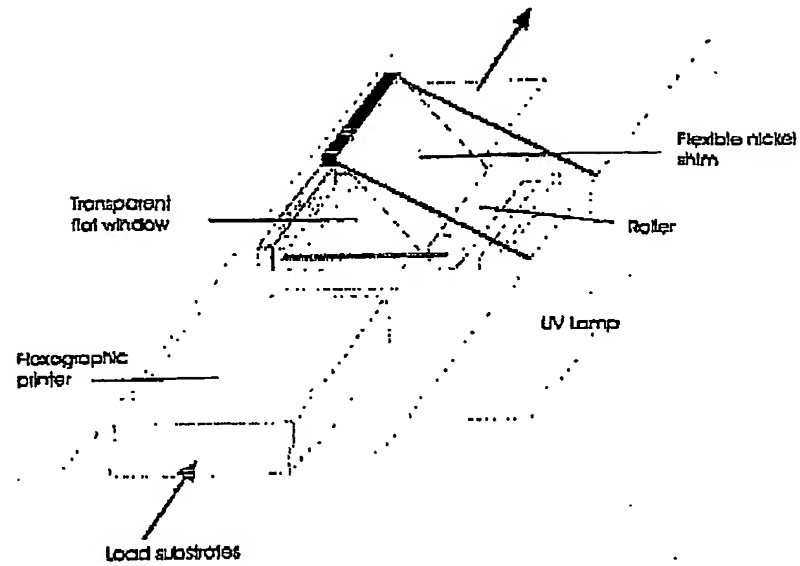

Figure 5 Flexible nickel or polymer shim onto glass embossing machine

The photopolymer must exhibit excellent release from a carrier film or a flexible shim (nickel or polymer) but show excellent adhesion to glass and ITO. This is critical to achieving a good fidelity copy of surface profile from the carrier film or shim on the glass substrate. There are two (or more) approaches. The first is to ensure that the carrier film or shim has a low surface energy (to form a non-stick coating). The second is to ensure that the photopolymer and the carrier film or shim have incompatible chemical groups at their surface. Possible carrier film or shim materials are

Polycarbonate
Polyester
PMMA
Nickel
Hot foil polymer
UV Lacquers

3. Additives to control surface energy and release.

Silicones can be used as an additive to reduce viscosity and modify release from various surfaces. They can be, for example, an acrylate or epoxy functionallized polydimethyl siloxane (PDMS) material. If used as part of a blend with monofunctional or bifunctional acrylate monomer, for example, they migrate to the interface and cause the cured film to be lower in surface energy.

Example of a Silicone Acrylate

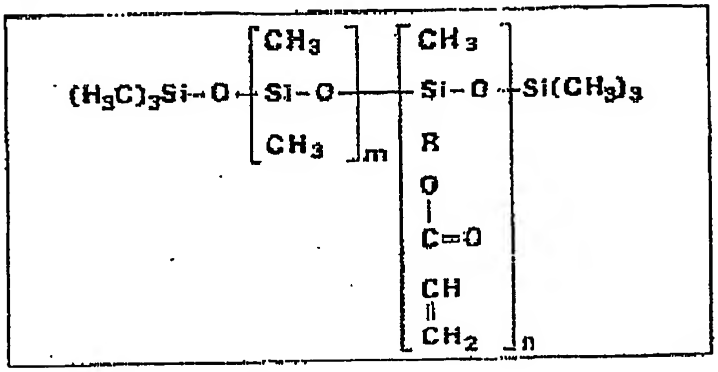

Figure 6 An example of a silicone acrylate

4. Surface treatable.

If the photopolymer blend does not have the correct surface energy to induce homeotropic alignment of the LC, it can be post treated with a coating.

5. Dielectric properties

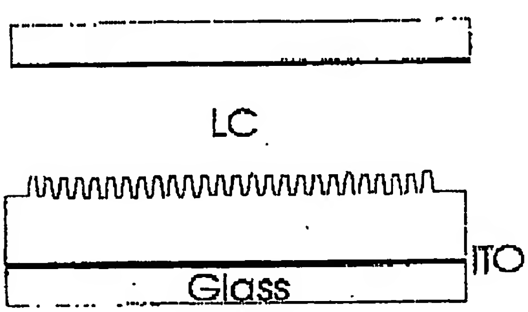

Figure 7 Schematic of an embossed grating within a ZBD cell.

Figure 7 shows a schematic of an embossed grating within a ZBD cell. A voltage is applied across the device. Some voltage is dropped across the LC and some across the grating. There are two ways to minimize the voltage dropped across the grating. First the total polymer thickness of the grating layer should be minimized. This is controlled by the viscosity of the material and the speed and pressure used during the embossing step. Secondly, the dielectric permittivity should be as high as possible.

Supply of photopolymer for ZBD Displays Limited

1. Business Opportunity:

With its unique proprietary bi-stable technology, ZBD is well positioned to participate in a significant portion of the LCD market for portable electronic devices, a market expected to exceed $20 billion by 2006. Current analysis of the various portable device applications comprising this market results in a $12 billion addressable market which includes everything from mobile phones, PDAs, handheld GPS, electronic books and web tablets, to electronic shelf edge labels, point of sale terminals, handheld games, toys and watches.

This addressable market represents more than 10 million square meters of displays to be manufactured in 2006 into which a ZBD proprietary grating could be integrated.

2. Manufacturing solutions:

The key difference between ZBD technology and existing LCDs is the incorporation of a diffraction grating on one of the internal glass surfaces of the display. The grating consists of a periodic array of grooves about 1 micron in pitch and 0.85 microns in height.

There are a number of options available to integrate ZBD's grating into an LCD at the manufacturing level. After careful analysis of these options, it has been determined that the transfer of our grating onto the glass substrates can be done most economically and at commercially acceptable throughputs via a UV photopolymer cast and cure process that we refer to as "embossing". We have demonstrated that this can be achieved using nickel or polymeric transfer surfaces or "shims".

Both of these methods have their own set of advantages and disadvantages. For example, a nickel shim will be more expensive than a polymeric shim, but it may be easier to use over and over again, potentially reaching levels similar to the CD industry at greater than 20,000 per replicas. On the other hand, polymeric shims could be manufactured very economically from Nickel masters, but the expected lifetime would be much lower than for nickel, potentially becoming a single-use consumable for LCD manufacturers. While the LCD industry boasts enormous sales figures, it is extremely price sensitive and margins are generally very low, with losses recorded by many manufacturers in the past 2 years. Quality of key components such as embossing shims, and overall yields from the embossing process will be critical. Any additional cost to the manufacturing process needs to be offset by very visible performance improvements that manufacturers, and ultimately consumers, will be willing to pay for.

4. Importance of photopolymer formulation.

The key ingredient to obtaining a high yield, reproducible manufacturing process is the photopolymer formulation. It must exhibit excellent release from the shim yet good adhesion to the substrate. Furthermore, since the photopolymer is in physical contact with the liquid crystal in the final display the physical, optical and chemical properties are of great important. Physical properties include low viscosity, fast cure, low odour and toxicity, low shrinkage and resistance to various solvents. Chemical properties include differential adhesion, correct surface energy for LC alignment (or be able to be treated) , and low ionic content. Optical properties include matching the refractive index to n_0 of the liquid crystal to minimise diffractive losses, and the minimisation of absorption and colouration. The electrical properties (such as the real and imaginary parts of the dielectric constant) determine, in part, the switching characteristics of the cell. Ionic content of the polymer will be detrimental to the switching and aging characteristics of the display.

5.0 Photopolymer properties

5.1 Release

It is critical to obtain photopolymers that will separate from the shim yet adhere to the substrate. There are a number possible shim materials. Optimised solutions are required for each possible material. They include

Nickel
Polycarbonate (plus hot foil layer?)
Polyester (plus hot foil layer?)
PMMA (plus hot foil layer?)
Carrier film 2 - lacquer
Carrier film 4 - lacquer
Carrier film 5 - lacquer

ZBD will supply quantities of shims for testing

5.2 Refractive Index

The refractive index should match n_0 of the liquid crystal, currently equal to 1.504. This condition minimises diffractive losses from within the device and improves brightness and contrast.

5.3 Optical absorption

The materials should be optically clear and show little or no absorption in the visible region of the spectrum.

5.4 Viscosity

The viscosity determines the thickness of embossed film for a given set of embossing parameters (such as pressure and speed) and ultimately determines the throughput of the embossing step which affects manufacturing cost. Ideally a viscosity of less than 200 cps is required.

5.5 Surface energy

The surface energy is important for two reasons. Firstly, it will impact on the adhesion properties to the glass and the release from the shim. Secondly, the material should induce homeotropic alignment of the liquid crystal. Examples of correct polar and dispersive components of the surface energy are:-

$\gamma_p = 8.6$ mN/m and $\gamma_d = 15.7$ mN/m.
$\gamma_p = 0.8$ mN/m and $\gamma_d = 25.1$ mN/m
$\gamma_p = 9.9$ mN/m and $\gamma_d = 14.8$ mN/m.

5.6 Shrinkage

Ideally there should be little or no shrinkage (<3%). Shrinkage reduces the amplitude of the embossed copy compared to that of the shim. This can be accounted for by making the grating amplitude larger on the shim. However, the degree of shrinkage must be uniform and repeatable over the area of the grating. Shrinkage will also distort the shape of the grating grooves. Again so long as the distortion is uniform and repeatable it can be accounted for by careful design of the shim. Ideally though the shape should be a faithful reproduction of the shim. Monomers tend to have low viscosity but high shrinkage, conversely oligomers have higher viscosity and lower volume shrinkage. In some instances release from the master grating is aided by some shrinkage.

5.7 Surface treatment capability

Currently, the grating material is treated . to lower the surface energy to induce homeotropic alignment of the liquid crystal.

5.8 Polymerisation speed

The required polymerisation speed is relatively slow compared to standard reel-to-reel processes. A 14 by 16 inch area of film 1 micron thick can be illuminated for several seconds to achieve cure. Further, the photopolymer system may be epoxy, vinyl or acrylate based.

5.10 Solvent compatibility

The film has to survive several solvent washes. Typical solvents are IPA, acetone, and the liquid crystal.

5.11 Ionic impurities.

The electrical switching of the LC in a ZBD device is sensitive to ions leeching from the photopolymer. Ionic content of the photopolymer should be minimised.

5.12 Dielectric constant

In order to decrease the operating voltage it is desirable to choose a photopolymer with a high dielectric constant. This reduces the voltage drop across the grating.

6.0 Scope of trial

In order of importance the formulation should be optimised in the following order

Release from shim
Refractive index
Viscosity
Surface energy
Shrinkage
Solvent compatibility

The trial may progress as follows. A number of photopolymer formulations will be blended that have low viscosity, are optically clear and have the correct refractive index. These should be tested for release against a number of materials that ZBD will supply. For example ZBD will supply a number of nickel shims, lengths of UV embossed carrier film, and lengths of hot foil embossed carrier film. Release tests can be performed in the following manor.

Clean ITO glass substrate
Place in UV Ozone chamber to oxides surface.
Place single drop of photopolymer onto the substrate
Laminate carrier film or shim (either pass through a set of rollers, or manually apply pressure)
Cure under UV lamp
Peel back the carrier film or shim and note degree of release.

Once a subset of materials show good release the surface energy should be measured. This can be performed by contact angle measurements (ZBD has this capability). The formulations should be adjusted to increase or lower the surface energy as required.

ZBD will test possible formulations for compatibility with surface treatment and solvents.

Shrinkage can be evaluated by taking cross-sectional SEMs of the shim and embossed copy. Careful inspection of grating shape and amplitude reveals effects of shrinkage. ZBD can perform these tests.

7.0 Successful outcome of trial.

Success criteria is defined as

1) The supply of sample quantities of at least one optimised photopolymer for each shim material that show excellent release.
2) Each optimised photopolymer should have the correct refractive index and viscosity
3) The surface energy should induce homeotropic alignment of the LC or the photopolymer should be treatable.
4) The photopolymers should be solvent resistant.

8.0 Schematics of possible embossing machines